

## CLAIMS

We Claim:

- 5           1.     A composition comprising core/shell nanocrystals, wherein:  
                  the nanocrystals comprise a core material and a shell material  
                  overcoating the core material, each of which is independently selected from a  
                  II/VI compound or a III/V compound,  
                  the band gap of the core material is less than the band gap of the  
10    shell material; and  
                  the thickness of the shell material is from 1 to about 15  
                  monolayers.
2.     The composition of Claim 1, wherein the thickness of the shell  
15    material is from 3 to about 15 monolayers.
3.     The composition of Claim 1, wherein the thickness of the shell  
                  material is from 5 to about 15 monolayers.
- 20           4.     The composition of Claim 1, wherein the core/shell nanocrystals  
                  exhibit a type-I band offset or a type-II band offset.
5.     The composition of Claim 1, wherein the core material is selected  
                  from CdSe, CdS, CdTe, ZnSe, ZnS, ZnTe, HgSe, HgS, HgTe, ZnO, CdO, GaAs,  
25    InAs, GaP, or InP;  
                  the shell material is selected from CdSe, CdS, CdTe, ZnSe, ZnS,  
                  ZnTe, HgSe, HgS, HgTe, ZnO, CdO, GaAs, InAs, GaP, or InP; and  
                  the shell material is different from the core material.
- 30           6.     The composition of Claim 1, wherein the core/shell nanocrystals  
                  comprise CdSe/CdS, CdSe/ZnSe, CdSe/ZnS, CdS/ZnS, CdTe/CdSe, CdTe/CdS,

CdTe/ZnTe, CdTe/ZnSe, CdTe/ZnS, ZnSe/ZnS, ZnTe/CdS, ZnTe/ZnSe, InAs/InP, InAs/CdSe, InAs/CdS, InAs/ZnS, InP/CdS, InP/ZnS, InP/ZnSe, InAs/InP/CdS, or a mixture thereof.

5           7.     The composition of Claim 1, wherein the as-prepared core/shell nanocrystals exhibit a photoluminescence quantum yield (PL QY) up to about 40%.

            8.     The composition of Claim 1, wherein the core/shell nanocrystals  
10    luminesce at a wavelength from about 400 to about 1000 nm.

            9.     The composition of Claim 1, wherein the core/shell nanocrystals exhibit a photoluminescence emission line characterized by a FWHM of about 50 nm or less.

15           10.    The composition of Claim 1, wherein the core/shell nanocrystals exhibit a photoluminescence emission line characterized by a FWHM of about 40 nm or less.

20           11.    The composition of Claim 1, wherein the core/shell nanocrystals exhibit a photoluminescence emission line characterized by a FWHM of about 28 nm or less when the core material comprises CdSe.

            12.    The composition of Claim 1, wherein the core/shell nanocrystals  
25    are characterized by a size distribution having a standard deviation no greater than about 15% of a mean diameter of the population of core/shell nanocrystals.

            13.    A light-emitting diode comprising the composition of Claim 1.

30           14.    A biological labeling agent comprising the composition of Claim 1.

15. A photoelectric device comprising the composition of Claim 1.
16. A solar cell comprising the composition of Claim 1.
- 5 17. A laser comprising the composition of Claim 1.
18. A composition comprising nanocrystalline, core/shell quantum shells, wherein:
- 10 the quantum shells comprise a core material and a shell material overcoating the core material;
- the core material comprises a stable, nanometer-sized inorganic solid;
- the shell material overcoating the core material is selected from a
- 15 II/VI compound or a III/V compound;
- the band gap of the core material is greater than the band gap of the shell material;
- the thickness of the shell material is from 1 to about 15 monolayers; and
- 20 the as-prepared quantum shells having the shell thickness greater than 1 monolayer exhibit a photoluminescence that is substantially limited to a bandgap emission, with a photoluminescence quantum yield (PL QY) up to about 20%.
- 25 19. The composition of Claim 18, wherein the core material comprises a II/VI compound or a III/V compound.
20. The composition of Claim 18, wherein photogenerated excitons are radially confined in the shell of the quantum shells.
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21. The composition of Claim 18, wherein the quantum shells exhibit a type-I band offset.

22. The composition of Claim 18, wherein the core of the quantum shells comprise an insulator.

23. The composition of Claim 18, wherein quantum shells comprise CdS/CdSe, CdS/InP, CdS/CdTe, ZnS/CdS, ZnS/CdSe, ZnS/ZnSe, ZnS/CdTe, ZnSe/CdSe, ZnSe/InP, CdS/InAs, CdSe/InAs, ZnSe/InAs, ZnS/InAs, InP/InAs, or a mixture thereof.

24. The composition of Claim 18, wherein the quantum shells luminesce at a wavelength from about 400 to about 1000 nm.

25. The composition of Claim 18, wherein the quantum shells exhibit a photoluminescence emission line characterized by a FWHM of about 50 nm or less.

26. The composition of Claim 18, wherein the quantum shells exhibit a photoluminescence emission line characterized by a FWHM of about 40 nm or less.

27. The composition of Claim 18, wherein the quantum shells exhibit a photoluminescence emission line characterized by a FWHM of about 35 nm or less.

28. The composition of Claim 18, wherein the quantum shells are characterized by a size distribution having a standard deviation no greater than about 15% of a mean diameter of the population of core/shell nanocrystals.

29. A light-emitting diode comprising the composition of Claim 18.

30. A biological labeling agent comprising the composition of Claim 18.
- 5 31. A photoelectric device comprising the composition of Claim 18.
32. A laser comprising the composition of Claim 18.
33. A composition comprising nanocrystalline, core/shell/shell  
10 quantum wells, wherein:  
the quantum wells comprise a core material, a first shell material overcoating the core material, and a second shell material overcoating the first shell material;  
the core material comprises a stable, nanometer-sized inorganic  
15 solid;  
the first shell material and the second shell material are independently selected from a II/VI compound or a III/V compound;  
the band gap of the first shell material is less than the band gap of the core material and less than the band gap of the second shell material; and  
20 the as-prepared quantum wells exhibit a photoluminescence that is substantially limited to a bandgap emission, with a photoluminescence quantum yield (PL QY) up to about 50%.
34. The composition of Claim 33, wherein the core material comprises  
25 a II/VI compound or a III/V compound.
35. The composition of Claim 33, wherein the core material comprises an insulator.
- 30 36. The composition of Claim 33, wherein the quantum wells comprise CdS/CdSe/CdS, CdS/CdSe/ZnSe, CdS/CdSe/ZnS, ZnSe/CdSe/CdS,

ZnSe/CdSe/ZnSe, ZnSe/CdSe/ZnS, ZnS/CdSe/ZnS, ZnS/CdSe/CdS,  
 ZnS/CdSe/ZnSe, ZnS/CdS/ZnS, ZnS/ZnSe/ZnS, CdS/InP/CdS, CdS/InP/ZnSe,  
 CdS/InP/ZnS, ZnSe/InP/ZnSe, ZnSe/InP/CdS, ZnSe/InP/ZnS, ZnS/InP/ZnS,  
 ZnS/InP/CdS, ZnS/InP/ZnSe, CdS/InAs/CdS, CdS/InAs/ZnSe, CdS/InAs/ZnS,  
 5 ZnSe/InAs/ZnSe, ZnSe/InAs/CdS, ZnSe/InAs/ZnS, ZnS/InAs/ZnS,  
 ZnS/InAs/CdS, ZnS/InAs/ZnSe, CdSe/InAs/CdSe, CdSe/InAs/CdS,  
 CdSe/InAs/ZnS, CdSe/InAs/ZnSe, InAs/InP/CdS, or a mixture thereof.

37. The composition of Claim 33, wherein the core material and the  
 10 second shell material are the same.

38. A light-emitting diode comprising the composition of Claim 33.

39. A biological labeling agent comprising the composition of Claim  
 15 33.

40. A photoelectric device comprising the composition of Claim 33.

41. A laser comprising the composition of Claim 33.  
 20

42. A composition comprising nanocrystalline, core/multiple shell  
 quantum wells, wherein:

the quantum wells comprise a core material, a first shell material  
 overcoating the core material, a second shell material overcoating the first shell  
 25 material, and optionally comprising additional shell materials sequentially  
 overcoating underlying shells;

the core material comprises a stable, nanometer-sized inorganic  
 solid;

the first shell material and the second shell material are  
 30 independently selected from a II/VI compound or a III/V compound;

any additional shells are independently selected from a II/VI compound or a III/V compound; and

the band gap of any shell material is less than the band gap of the both adjacent core or shell materials, or greater than the band gap of the both adjacent core or shell materials.

43. The composition of Claim 42, wherein the core material comprises a II/VI compound or a III/V compound.

44. The composition of Claim 42, wherein the core material of the quantum wells comprises an insulator.

45. A composition comprising radially-doped, core/multiple shell nanocrystals wherein:

the radially-doped nanocrystals comprise a core material, a first shell material overcoating the core material, a second shell material overcoating the first shell material, and a third shell material overcoating the second shell material;

the core material comprises a compound of the formula  $M^1_a E^1_b$ , wherein  $M^1$  is selected from a group II or group III metal;  $E^1$  is selected from a non-metal; and a and b are dictated by the stoichiometry of the compound;

the first shell material comprises a compound of the formula  $M^1_a M^2_c E^1_b$ , wherein  $M^2$  is selected from at least one transition metal;  $0 \leq c < a$ ; and  $M^2$  is different than  $M^1$ ;

the second shell material comprises a compound of the formula  $M^3_d M^4_f E^3_e$ , wherein  $M^3$  is selected from a group II or group III metal;  $M^4$  is selected from a transition metal, a rare earth metal, or a mixture thereof; d and e are dictated by the stoichiometry of the compound  $M^3_d E^3_e$ ; and  $0 \leq f < d$ ;

the third shell material comprises a compound of the formula  $M^5_g M^6_i E^5_h$ , wherein  $M^5$  is selected from a group II or group III metal;  $M^6$  is selected

from a transition metal, a rare earth metal, or a mixture thereof; g and h are dictated by the stoichiometry of the compound  $M_g^5E_h^5$ ; and  $0 \leq i < g$ ;

wherein the bandgap of the third shell material is greater than the bandgap of the core material, greater than the bandgap of the first shell material, and greater than the bandgap of the second shell materials; and

wherein the thicknesses of the first shell material, the second shell material, and the third shell material are independently varied between 0 and 15 monolayers.

46. The composition of Claim 45, wherein:

a) i)  $M^1$  is selected from Zn, Cd, or Hg, and  $E^1$  is selected from O, S, Se, or Te; or

ii)  $M^1$  is selected from Ga and In, and  $E^1$  is selected from N, P and As; and

b)  $M^2$  is selected from Mn, Fe, Co, Ni, Pd, Pt, Cu, Al, Ag, or Au, or a rare earth metal.

47. The composition of Claim 45, wherein  $M_a^1E_b^1$  is selected from CdSe, CdS, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, InAs, InP, GaAs, GaP, ZnO, CdO, HgO,  $In_2O_3$ ,  $TiO_2$ , or a rare earth oxide.

48. The composition of Claim 45, wherein the radially-doped, core/multiple shell nanocrystals comprise  $ZnSe/Zn_{a-c}M_c^2Se/ZnSe$ ,  $ZnSe/Zn_{a-c}M_c^2Se/ZnS$ ,  $ZnO/Zn_{a-c}M_c^2O/ZnO$ ,  $ZnO/Zn_{a-c}M_c^2O/ZnS$ ,  $TiO_2/Ti_{a-c}M_c^2O_2/TiO_2$ , and wherein  $M^2$  is selected from Mn, Fe, Co, Ni, Pd, Pt, Al, Cu, Ag, or Au, or a rare earth metal.

49. A composition comprising core/shell/shell dual-emitting nanocrystals, wherein:

the nanocrystals comprise a core material, a first shell material overcoating the core material, and a second shell material overcoating the first



shell material, each of which is independently selected from a II/VI compound or a III/V compound;

the band gap of the first shell material is greater than the band gap of the core material and greater than the band gap of the second shell material;

5 and

the as-prepared dual-emitting nanocrystals exhibit a photoluminescence comprising two bandgap emission peaks.

50. The composition of Claim 49, wherein the dual-emitting  
10 nanocrystals further comprise at least one additional shell material sequentially overcoating underlying shells, wherein:

the additional shell materials are independently selected from a II/VI compound or a III/V compound; and

the band gap of the additional shell materials are greater than the  
15 band gap of the second shell material.

51. A composition comprising core/shell/shell/shell dual-emitting nanocrystals, wherein:

the nanocrystals comprise a core material, a first shell material  
20 overcoating the core material, a second shell material overcoating the first shell material, and a third shell material overcoating the second shell material, each of which is independently selected from a II/VI compound or a III/V compound;

the band gap of the first shell material and the band gap of the  
third shell material are less than the band gap of the core material and are less  
25 than the band gap of the second shell material; and

the as-prepared dual-emitting nanocrystals exhibit a photoluminescence comprising two bandgap emissions.

52. The composition of Claim 51, wherein the dual-emitting  
30 nanocrystals further comprise at least one additional shell material sequentially overcoating underlying shells, wherein:

the additional shell materials are independently selected from a II/VI compound or a III/V compound; and

the band gap of the additional shell materials are greater than the band gap of the second shell material.

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53. A composition comprising core/multiple shell nanocrystals, wherein:

the nanocrystals comprise a core material, a first shell material overcoating the core material, a second shell material overcoating the first shell material, a third shell material overcoating the second shell material, a fourth shell material overcoating the third shell material, and optionally additional shells overcoating underlying shells, each of which is independently selected from a II/VI compound or a III/V compound;

the band gap of any shell material is less than the band gap of the both adjacent core or shell materials, or greater than the band gap of the both adjacent core or shell materials.

54. A population of nanocrystals comprising a plurality of nanocrystals, wherein:

each nanocrystal comprises a core material and the shell material overcoating the core material, each of which is independently selected from a II/VI compound or a III/V compound,

wherein the band gap of the core material is less than the band gap of the shell material;

wherein the population of nanocrystals is substantially monodisperse; and

wherein the plurality of nanocrystals exhibit a photoluminescence quantum yield (PL QY) of greater than or equal to about 20%.

55. The population of nanocrystals of Claim 54, wherein:

the core material is selected from CdSe, CdS, CdTe, ZnSe, ZnS, ZnTe, HgSe, HgS, HgTe, ZnO, CdO, GaAs, InAs, GaP, or InP;

the shell material is selected from CdSe, CdS, CdTe, ZnSe, ZnS, ZnTe, HgSe, HgS, HgTe, ZnO, CdO, GaAs, InAs, GaP, or InP; and

5 the shell material is different from the core material.

56. The population of nanocrystals of Claim 54, wherein the plurality of nanocrystals exhibit a photoluminescence quantum yield (PL QY) of greater than or equal to about 30%.

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57. The population of nanocrystals of Claim 54, wherein the plurality of cores has a size distribution having a standard deviation no greater than about 20% of a mean diameter of the population.

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58. A method for preparing core/shell nanocrystals having the formula  $M^1X^1/M^2X^2$ , comprising:

a) providing a solution of core nanocrystals of the formula  $M^1X^1$ ;

20 b) forming a first monolayer of a shell material  $M^2X^2$  by contacting the core nanocrystals, in an alternating manner, with a cation ( $M^2$ ) precursor solution in an amount effective to form a monolayer of the cation, and an anion ( $X^2$ ) precursor solution in an amount effective to form a monolayer of the anion; and

25 c) optionally forming subsequent monolayers of shell material  $M^2X^2$  by contacting the core/shell nanocrystals, in an alternating manner, with a cation ( $M^2$ ) precursor solution in an amount effective to form a monolayer of the cation, and an anion ( $X^2$ ) precursor solution in an amount effective to form a monolayer of the anion;

30 wherein  $M^1X^1$  comprises a stable, nanometer-sized inorganic solid;

wherein  $M^2X^2$  is selected from a II/VI compound or a III/V compound; and

wherein  $M^1X^1$  and  $M^2X^2$  are different.

5            59.    A method for preparing core/shell nanocrystals having the formula  $M^1X^1/M^2X^2$ , comprising:

- a)        providing a solution of core nanocrystals of the formula  $M^1X^1$ ;
- b)        forming at least one monolayer of a shell material  $M^2X^2$  by  
10        contacting the core nanocrystals, in an alternating manner, with a cation ( $M^2$ ) precursor solution in an amount effective to form a monolayer of the cation, and an anion ( $X^2$ ) precursor solution in an amount effective to form a monolayer of the anion;

15            wherein  $M^1X^1$  comprises a stable, nanometer-sized inorganic solid;

wherein  $M^2X^2$  is selected from a II/VI compound or a III/V compound; and

wherein  $M^1X^1$  and  $M^2X^2$  are different.

20            60.    The method of Claim 59,  $M^2X^2$  comprises a II/VI compound or a III/V compound.

25            61.    The method of Claim 59, wherein the cation ( $M^2$ ) precursor solution is contacted with the core nanocrystals before the anion ( $X^2$ ) precursor solution is contacted with the core nanocrystals.

30            62.    The method of Claim 59, wherein the anion ( $X^2$ ) precursor solution is contacted with the core nanocrystals before the cation ( $M^2$ ) precursor solution is contacted with the core nanocrystals.

63. The method of Claim 59, further comprising purifying the core/shell nanocrystals.

64. The method of Claim 59, wherein  $M^1X^1$  and  $M^2X^2$  are  
5 independently selected from CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, ZnO, CdO, InP, InAs, GaAs, or GaP.

65. The method of Claim 59, wherein the cation precursor solution comprises a metal oxide, a metal halide, a metal nitride, a metal ammonia  
10 complex, a metal amine, a metal amide, a metal imide, a metal carboxylate, a metal acetylacetonate, a metal dithiolate, a metal carbonyl, a metal cyanide, a metal isocyanide, a metal nitrile, a metal peroxide, a metal hydroxide, a metal hydride, a metal ether complex, a metal diether complex, a metal triether complex, a metal carbonate, a metal phosphate, a metal nitrate, a metal nitrite, a  
15 metal sulfate, a metal alkoxide, a metal siloxide, a metal thiolate, a metal dithiolate, a metal disulfide, a metal carbamate, a metal dialkylcarbamate, a metal pyridine complex, a metal bipyridine complex, a metal phenanthroline complex, a metal terpyridine complex, a metal diamine complex, a metal triamine complex, a metal diimine, a metal pyridine diimine, a metal pyrazolylborate, a metal  
20 bis(pyrazolyl)borate, a metal tris(pyrazolyl)borate, a metal nitrosyl, a metal thiocarbamate, a metal diazabutadiene, a metal dithiocarbamate, a metal dialkylacetamide, a metal dialkylformamide, a metal formamidinate, a metal phosphine complex, a metal arsine complex, a metal diphosphine complex, a metal diarsine complex, a metal oxalate, a metal imidazole, a metal pyrazolate, a  
25 metal-Schiff base complex, a metal porphyrin, a metal phthalocyanine, a metal subphthalocyanine, a metal picolinate, a metal piperidine complex, a metal pyrazolyl, a metal salicylaldehyde, a metal ethylenediamine, a metal triflate compound, or any combination thereof.

30 66. The method of Claim 59, wherein the cation precursor comprises a metal oxide, a metal carbonate, a metal bicarbonate, a metal sulfate, a metal

sulfite, a metal phosphate, metal phosphite, a metal halide, a metal carboxylate, a metal hydroxide, a metal alkoxide, a metal thiolate, a metal amide, a metal imide, a metal alkyl, a metal aryl, a metal coordination complex, a metal solvate, a metal salt, or a combination thereof.

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67. The method of Claim 59, wherein the cation precursor solution optionally comprises a ligand selected from a fatty acid, an fatty amine, a phosphine, a phosphine oxide, a phosphonic acid, a phosphinic acid, a sulphonic acid, or any combination thereof, any one of which having up to about 30 carbon atoms.

10

68. The method of Claim 59, wherein the anion precursor comprises an element, a covalent compound, an ionic compound, or a combination thereof.

15

69. A method for preparing core/shell/shell nanocrystals having the formula  $M^1X^1/M^2X^2/M^3X^3$  comprising:

a) providing a solution of core nanocrystals of the formula  $M^1X^1$ ;

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b) forming at least one monolayer of a first shell material  $M^2X^2$  by contacting the core nanocrystals, in an alternating manner, with a first cation ( $M^2$ ) precursor solution in an amount effective to form a monolayer of the first cation, and a first anion ( $X^2$ ) precursor solution in an amount effective to form a monolayer of the first anion; and

25

c) forming at least one monolayer of a second shell material  $M^3X^3$  by contacting the core nanocrystals, in an alternating manner, with a second cation ( $M^3$ ) precursor solution in an amount effective to form a monolayer of the second cation, and an second anion ( $X^3$ ) precursor solution in an amount effective to form a monolayer of the first anion;

30

wherein  $M^1X^1$  comprises a stable, nanometer-sized inorganic solid;

wherein  $M^2X^2$  and  $M^3X^3$  are independently selected from a II/VI compound or a III/V compound; and

wherein  $M^1X^1$ ,  $M^2X^2$ , and  $M^3X^3$  are different.

5           70. The method of Claim 69,  $M^2X^2$  comprises a II/VI compound or a III/V compound.

71. The method of Claim 69, wherein the cation ( $M^2$ ) precursor solution is contacted with the core nanocrystals before the anion ( $X^2$ ) precursor  
10 solution is contacted with the core nanocrystals.

72. The method of Claim 69, wherein the anion ( $X^2$ ) precursor solution is contacted with the core nanocrystals before the cation ( $M^2$ ) precursor solution is contacted with the core nanocrystals.

15           73. The method of Claim 69, further comprising purifying the core/shell nanocrystals.

74. The method of Claim 69, wherein  $M^1X^1$ ,  $M^2X^2$ , and  $M^3X^3$  are  
20 independently selected from CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, ZnO, CdO, InP, InAs, GaAs, or GaP.

75. The method of Claim 69, wherein the cation precursor solution comprises a metal oxide, a metal halide, a metal nitride, a metal ammonia  
25 complex, a metal amine, a metal amide, a metal imide, a metal carboxylate, a metal acetylacetonate, a metal dithiolate, a metal carbonyl, a metal cyanide, a metal isocyanide, a metal nitrile, a metal peroxide, a metal hydroxide, a metal hydride, a metal ether complex, a metal diether complex, a metal triether complex, a metal carbonate, a metal phosphate, a metal nitrate, a metal nitrite, a  
30 metal sulfate, a metal alkoxide, a metal siloxide, a metal thiolate, a metal dithiolate, a metal disulfide, a metal carbamate, a metal dialkylcarbamate, a metal

pyridine complex, a metal bipyridine complex, a metal phenanthroline complex, a metal terpyridine complex, a metal diamine complex, a metal triamine complex, a metal diimine, a metal pyridine diimine, a metal pyrazolylborate, a metal bis(pyrazolyl)borate, a metal tris(pyrazolyl)borate, a metal nitrosyl, a metal  
5 thiocarbamate, a metal diazabutadiene, a metal dithiocarbamate, a metal dialkylacetamide, a metal dialkylformamide, a metal formamidinate, a metal phosphine complex, a metal arsine complex, a metal diphosphine complex, a metal diarsine complex, a metal oxalate, a metal imidazole, a metal pyrazolate, a metal-Schiff base complex, a metal porphyrin, a metal phthalocyanine, a metal  
10 subphthalocyanine, a metal picolinate, a metal piperidine complex, a metal pyrazolyl, a metal salicylaldehyde, a metal ethylenediamine, a metal triflate compound, or any combination thereof.

76. The method of Claim 69, wherein the cation precursor comprises a  
15 metal oxide, a metal carbonate, a metal bicarbonate, a metal sulfate, a metal sulfite, a metal phosphate, metal phosphite, a metal halide, a metal carboxylate, a metal hydroxide, a metal alkoxide, a metal thiolate, a metal amide, a metal imide, a metal alkyl, a metal aryl, a metal coordination complex, a metal solvate, a metal salt, or a combination thereof.

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77. The method of Claim 69, wherein the cation precursor solution optionally comprises a ligand selected from a fatty acid, an fatty amine, a phosphine, a phosphine oxide, a phosphonic acid, a phophinic acid, a sulphonic acid, or any combination thereof, any one of which having up to about 30 carbon  
25 atoms.

78. The method of Claim 69, wherein the anion precursor comprises an element, a covalent compound, an ionic compound, or a combination thereof.

79. A method for preparing radially-doped core/shell/shell  
30 nanocrystals having the formula  $M^1_xE_y/M^1_{x-z}M^2_zE_y/M^1_{x-q}M^3_qE_y$ , comprising:



a) providing a solution of core nanocrystals of the formula  $M^1_xE_y$ , wherein  $M^1$  is selected from a metal, E is selected from a non-metal, and x and y are dictated by the stoichiometry of the compound;

b) forming at least one monolayer of a doped first shell material of the formula  $M^1_{x-z}M^2_zE_y$  by contacting the core nanocrystals, in an alternating manner, with a cation precursor solution in an amount effective to form a monolayer of the first cation doped with the second cation, and a first anion ( $X^2$ ) precursor solution in an amount effective to form a monolayer of the first anion;

wherein the cation precursor solution comprises a first cation ( $M^1$ ) precursor, a second cation ( $M^2$ ) precursor, or a combination thereof, and

wherein  $M^2$  is selected from a transition metal or a mixture thereof,  $0 \leq z < x$ , and  $M^2$  is different than  $M^1$ ;

c) forming at least one monolayer of a second shell material of the formula  $M^1_{x-q}M^3_qE_y$  by contacting the core/shell nanocrystals, in an alternating manner, with a first cation precursor solution in an amount effective to form a monolayer of the first cation, and an second anion ( $X^3$ ) precursor solution in an amount effective to form a monolayer of the first anion;

wherein the first cation precursor solution optionally comprises a third cation ( $M^3$ ) precursor selected from a transition metal, a rare earth metal, or a mixture thereof; and

wherein  $0 \leq q \leq x$ , and x is not equal to q when  $M^2$  is the same as  $M^3$ ; and

d) optionally repeating steps b and c to form additional shells overcoating the second shell.

80. The method of Claim 79, wherein  $M^1E$  is selected from a II/VI compound or a III/V compound.

81. The method of Claim 79, wherein q is 0.

82. A composition comprising core/shell nanocrystals having the formula  $M^1X^1/M^2X^2$ , prepared by the method of:

a) providing a solution of core nanocrystals of the formula  
5  $M^1X^1$ ;

b) forming a first monolayer of a shell material  $M^2X^2$  by contacting the core nanocrystals, in an alternating manner, with a cation ( $M^2$ ) precursor solution in an amount effective to form a monolayer of the cation, and an anion ( $X^2$ ) precursor solution in an amount effective to form a monolayer of  
10 the anion; and

c) optionally forming subsequent monolayers of shell material  $M^2X^2$  by contacting the core/shell nanocrystals, in an alternating manner, with a cation ( $M^2$ ) precursor solution in an amount effective to form a monolayer of the cation, and an anion ( $X^2$ ) precursor solution in an amount  
15 effective to form a monolayer of the anion;

wherein the cation precursor solution optionally contains at least one ligand, and wherein the anion precursor solution optionally contains at least one ligand;

wherein  $M^1X^1$  comprises a stable, nanometer-sized inorganic  
20 solid;

wherein  $M^2X^2$  is selected from a II/VI compound or a III/V compound; and

wherein  $M^1X^1$  and  $M^2X^2$  are different.

25 83. A composition comprising radially-doped, core/multiple shell nanocrystals, comprising:

1) a core material having the formula  $M^1_{a-c}M^2_cE^1_b$ , wherein:

a)  $M^1$  is selected from a metal,  $E^1$  is selected from a non-metal, and a and b are dictated by the stoichiometry of the compound  
30  $M^1_aE^1_b$ ;

- b)  $M^2$  is selected from a transition metal, a rare earth metal, or a mixture thereof; and  $M^2$  is different than  $M^1$ ; and
- c)  $0 \leq c < a$ ;
- 2) an optional first shell material overcoating the core material,  
 5 having the formula  $M^3_d M^4_f E^3_e$ , wherein:
- a)  $M^3$  is selected from a metal,  $E^3$  is selected from a non-metal, and d and e are dictated by the stoichiometry of the compound  $M^3_d E^3_e$ ;
- b)  $M^4$  is selected from a transition metal, a rare earth metal,  
 10 or a mixture thereof; and  $M^4$  is different than  $M^3$ ; and
- c)  $0 \leq f < d$ ;
- 3) an optional second shell material overcoating the optional first shell material, having the formula  $M^5_g M^6_i E^5_h$ , wherein:
- a)  $M^5$  is selected from a metal,  $E^5$  is selected from a non-  
 15 metal, and g and h are dictated by the stoichiometry of the compound  $M^5_g E^5_h$ ;
- b)  $M^6$  is selected from a transition metal, a rare earth metal, or a mixture thereof; and  $M^6$  is different than  $M^5$ ; and
- c)  $0 \leq i < g$ ;
- 20 4) an optional third shell material overcoating the optional second shell material, having the formula  $M^7_j M^8_l E^7_k$ , wherein:
- a)  $M^7$  is selected from a metal,  $E^7$  is selected from a non-metal, and j and k are dictated by the stoichiometry of the compound  $M^7_j E^7_k$ ;
- 25 b)  $M^8$  is selected from a transition metal, a rare earth metal, or a mixture thereof; and  $M^8$  is different than  $M^7$ ; and
- c)  $0 \leq l < j$ ; and
- 5) an optional fourth shell material overcoating the optional third shell material, having the formula  $M^9_m M^{10}_o E^9_n$ , wherein:

a)  $M^9$  is selected from a metal,  $E^9$  is selected from a non-metal, and m and n are dictated by the stoichiometry of the compound  $M_m^9E_n^9$ ;

b)  $M^{10}$  is selected from a transition metal, a rare earth metal, or a mixture thereof; and  $M^{10}$  is different than  $M^9$ ; and

c)  $0 \leq o < m$ .

84. The composition of Claim 83, wherein  $M_a^1E_b^1$ ,  $M_d^3E_e^3$ ,  $M_g^5E_h^5$ ,  $M_j^7E_k^7$ , and  $M_m^9E_n^9$  are independently selected from a II/VI compound or a III/V compound.

85. The composition of Claim 83, wherein the thickness of the first shell material, the second shell material, the third shell, and the fourth shell material are independently varied between 1 and about 15 monolayers.

86. The composition of Claim 83, wherein the band gap of any shell material is less than the band gap of the both adjacent core or shell materials, or greater than the band gap of the both adjacent core or shell materials.

87. The composition of Claim 83, wherein:

a) i)  $M^1$ ,  $M^3$ ,  $M^5$ ,  $M^7$ , and  $M^9$  are independently selected from Zn, Cd, or Hg, and  $E^1$ ,  $E^3$ ,  $E^5$ ,  $E^7$ , and  $E^9$  are independently selected from O, S, Se, or Te; or

ii)  $M^1$ ,  $M^3$ ,  $M^5$ ,  $M^7$ , and  $M^9$  are independently selected from Ga and In, and  $E^1$ ,  $E^3$ ,  $E^5$ ,  $E^7$ , and  $E^9$  are independently selected from N, P and As; and

b)  $M^2$ ,  $M^4$ ,  $M^6$ ,  $M^8$ , and  $M^{10}$  are independently selected from Mn, Fe, Co, Ni, Pd, Pt, Cu, Al, Ag, or Au, or a rare earth metal.

88. The composition of Claim 83, wherein  $M_a^1E_b^1$ ,  $M_d^3E_e^3$ ,  $M_g^5E_h^5$ ,  $M_j^7E_k^7$ , and  $M_m^9E_n^9$  are independently selected from CdSe, CdS, CdTe, ZnS,

ZnSe, ZnTe, HgS, HgSe, HgTe, InAs, InP, GaAs, GaP, ZnO, CdO, HgO, In<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, or a rare earth oxide.

89. The composition of Claim 83, wherein the nanocrystals have the  
5 formula  $M^1_{a-c}M^2_cE^1_b$ .

90. The composition of Claim 83, wherein the nanocrystals have the  
formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e$ .

10 91. The composition of Claim 83, wherein the nanocrystals have the  
formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e/M^5_{g-i}M^6_iE^5_h$ .

92. The composition of Claim 83, wherein:  
a) the nanocrystals comprise a core material, a first shell material,  
15 and a second material; and have the formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e/M^5_{g-i}M^6_iE^5_h$ ; and  
b) the nanocrystals comprise ZnSe/Zn<sub>d-f</sub>M<sup>4</sup><sub>f</sub>Se/ZnSe, ZnSe/Zn<sub>d-f</sub>M<sup>4</sup><sub>f</sub>Se/ZnS, ZnO/Zn<sub>d-f</sub>M<sup>4</sup><sub>f</sub>O/ZnO, ZnO/Zn<sub>d-f</sub>M<sup>4</sup><sub>f</sub>O/ZnS, TiO<sub>2</sub>/Ti<sub>d-f</sub>M<sup>4</sup><sub>f</sub>O<sub>2</sub>/TiO<sub>2</sub>,  
and wherein M<sup>4</sup> is selected from Mn, Fe, Co, Ni, Pd, Pt, Cu, Al, Ag, or Au, or a  
20 rare earth metal.

93. The composition of Claim 83, wherein the nanocrystals have the  
formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e/M^5_{g-i}M^6_iE^5_h/M^7_{j-l}M^8_lE^7_k$ .

25 94. The composition of Claim 83, wherein the nanocrystals have the  
formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e/M^5_{g-i}M^6_iE^5_h/M^7_{j-l}M^8_lE^7_k$ .

95. The composition of Claim 83, wherein the nanocrystals have the  
formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e/M^5_{g-i}M^6_iE^5_h/M^7_{j-l}M^8_lE^7_k/M^9_{m-o}M^{10}_oE^9_n$ .

30

96. A method for preparing radially-doped core/multiple shell nanocrystals comprising a doped core material having the formula  $M^1_{a-c}M^2_cE^1_b$ , an optional doped first shell material having the formula  $M^3_{d-f}M^4_fE^3_e$  and overcoating the core material, an optional doped second shell material having the formula  $M^5_{g-i}M^6_iE^5_h$  and overcoating the first core material, an optional doped third shell material having the formula  $M^7_{j-l}M^8_lE^7_k$  and overcoating the second core material, and an optional doped fourth shell material having the formula  $M^9_{m-o}M^{10}_oE^9_n$  and overcoating the third core material, comprising:

a) providing a solution of core nanocrystals of the formula  $M^1_aE^1_b$ , wherein  $M^1$  is selected from a metal,  $E^1$  is selected from a non-metal, and a and b are dictated by the stoichiometry of the compound;

b) optionally forming at least one monolayer of a doped core material of the formula  $M^1_{a-c}M^2_cE^1_b$  by contacting the nanocrystals, in an alternating manner, with a first cation precursor solution in an amount effective to form a monolayer of a first cation  $M^1$ , optionally doped with a second cation  $M^2$ , and a first anion ( $E^1$ ) precursor solution in an amount effective to form a monolayer of the first anion;

wherein the first cation precursor solution comprises a first cation ( $M^1$ ) precursor and an optional second cation ( $M^2$ ) precursor; and

wherein  $M^2$  is selected from a transition metal, a rare earth metal, or a mixture thereof;  $M^2$  is different than  $M^1$ ; and  $0 \leq c < a$ ;

c) optionally forming at least one monolayer of a doped first shell material of the formula  $M^3_{d-f}M^4_fE^3_e$  by contacting the nanocrystals, in an alternating manner, with a second cation precursor solution in an amount effective to form a monolayer of a third cation  $M^3$ , optionally doped with a fourth cation  $M^4$ , and a second anion ( $E^3$ ) precursor solution in an amount effective to form a monolayer of the second anion;

wherein the second cation precursor solution comprises a third cation ( $M^3$ ) precursor and an optional fourth cation ( $M^4$ ) precursor; and

wherein  $M^3$  is selected from a metal,  $E^3$  is selected from a non-metal, and d and e are dictated by the stoichiometry of the compound  $M^3_dE^3_e$ ;

5 wherein  $M^4$  is independently selected from a transition metal, a rare earth metal, or a mixture thereof;  $M^4$  is different than  $M^3$ ; and  $0 \leq f < d$ ;

d) optionally repeating step c to form optional doped shells  $M^5_g$ ,  $M^6_iE^5_h$ ,  $M^7_{j-l}M^8_lE^7_k$ , and  $M^9_{m-o}M^{10}_oE^9_n$ , wherein  $M^5$ ,  $M^7$ , and  $M^9$  are independently selected from a metal;  $M^6$ ,  $M^8$ , and  $M^{10}$  are independently selected from a transition metal, a rare earth metal, or a mixture thereof;  $E^5$ ,  $E^7$ , and  $E^9$  are independently selected from a non-metal; g and h are dictated by the stoichiometry of the compound  $M^5_gE^5_h$ ; j and k are dictated by the stoichiometry of the compound  $M^7_jE^7_k$ , m and n are dictated by the stoichiometry of the compound  $M^9_mE^9_n$ ;  $0 \leq i < g$ ;  $0 \leq l < j$ ; and  $0 \leq o < m$ .

15

97. The method of Claim 96, wherein  $M^1_aE^1_b$ ,  $M^3_dE^3_e$ ,  $M^5_gE^5_h$ ,  $M^7_jE^7_k$ , and  $M^9_mE^9_n$  are independently selected from a II/VI compound or a III/V compound.

20 98. The method of Claim 96, wherein the thickness of the first shell material, the second shell material, the third shell, and the fourth shell material are independently varied between 1 and about 15 monolayers.

25 99. The method of Claim 96, wherein the band gap of any shell material is less than the band gap of the both adjacent core or shell materials, or greater than the band gap of the both adjacent core or shell materials.

100. The method of Claim 96, wherein:

30 a) i)  $M^1$ ,  $M^3$ ,  $M^5$ ,  $M^7$ , and  $M^9$  are independently selected from Zn, Cd, or Hg, and  $E^1$ ,  $E^3$ ,  $E^5$ ,  $E^7$ , and  $E^9$  are independently selected from O, S, Se, or Te; or

ii)  $M^1$ ,  $M^3$ ,  $M^5$ ,  $M^7$ , and  $M^9$  are independently selected from Ga and In, and  $E^1$ ,  $E^3$ ,  $E^5$ ,  $E^7$ , and  $E^9$  are independently selected from N, P and As; and

b)  $M^2$ ,  $M^4$ ,  $M^6$ ,  $M^8$ , and  $M^{10}$  are independently selected from Mn,  
5 Fe, Co, Ni, Pd, Pt, Cu, Al, Ag, or Au, or a rare earth metal.

101. The method of Claim 96, wherein  $M^1_a E^1_b$ ,  $M^3_d E^3_e$ ,  $M^5_g E^5_h$ ,  $M^7_j E^7_k$ ,  
and  $M^9_m E^9_n$  are independently selected from CdSe, CdS, CdTe, ZnS, ZnSe, ZnTe,  
HgS, HgSe, HgTe, InAs, InP, GaAs, GaP, ZnO, CdO, HgO,  $In_2O_3$ ,  $TiO_2$ , or a rare  
10 earth oxide.

102. The method of Claim 96, wherein the nanocrystals have the  
formula  $M^1_{a-c} M^2_c E^1_b$ .

15 103. The method of Claim 96, wherein the nanocrystals have the  
formula  $M^1_{a-c} M^2_c E^1_b / M^3_{d-f} M^4_f E^3_e$ .

104. The method of Claim 96, wherein the nanocrystals have the  
formula  $M^1_{a-c} M^2_c E^1_b / M^3_{d-f} M^4_f E^3_e / M^5_{g-i} M^6_i E^5_h$ .

20

105. The method of Claim 96, wherein:

a) the nanocrystals comprise a core material, a first shell material,  
and a second material; and have the formula  $M^1_{a-c} M^2_c E^1_b / M^3_{d-f} M^4_f E^3_e / M^5_{g-i} M^6_i E^5_h$ ; and

25 b) the nanocrystals comprise  $ZnSe/Zn_{d-f} M^4_f Se/ZnSe$ ,  $ZnSe/Zn_{d-f} M^4_f Se/ZnS$ ,  $ZnO/Zn_{d-f} M^4_f O/ZnO$ ,  $ZnO/Zn_{d-f} M^4_f O/ZnS$ ,  $TiO_2/Ti_{d-f} M^4_f O_2/TiO_2$ ,  
and wherein  $M^4$  is selected from Mn, Fe, Co, Ni, Pd, Pt, Cu, Al, Ag, or Au, or a  
rare earth metal.

30 106. The method of Claim 96, wherein the nanocrystals have the  
formula  $M^1_{a-c} M^2_c E^1_b / M^3_{d-f} M^4_f E^3_e / M^5_{g-i} M^6_i E^5_h / M^7_{j-l} M^8_l E^7_k$ .



107. The method of Claim 96, wherein the nanocrystals have the formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e/M^5_{g-i}M^6_iE^5_h/M^7_{j-l}M^8_lE^7_k$ .

5            108. The method of Claim 96, wherein the nanocrystals have the formula  $M^1_{a-c}M^2_cE^1_b/M^3_{d-f}M^4_fE^3_e/M^5_{g-i}M^6_iE^5_h/M^7_{j-l}M^8_lE^7_k/M^9_{m-o}M^{10}_oE^9_n$ .